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(54) **Austenitic heat-resistant alloys**

(57) An austenitic heat-resistant alloy consisting of (by weight): 0.02–0.15% C, 0.3–2.0% Si, 0.3–1.5% Mn, 18–25% Cr, 20.5–50% Ni, 0.5–3.0% Mo, 0.03–0.3% Ti, 0.05–0.6% Nb, 0.003–0.01% B, no more than 0.04% P, and no more than 0.005% S, with the balance being iron and unavoidable impurities, and satisfying the conditions  $Nb/Ti = 0.5-3$  (atomic ratio) and  $(Nb + Ti)/(C + N) = 0.2-0.85$  (atomic ratio).

The alloy is particularly useful as a boiler material, and shows excellent strength and corrosion resistance at elevated temperatures as well as excellent weldability.

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FIG.1

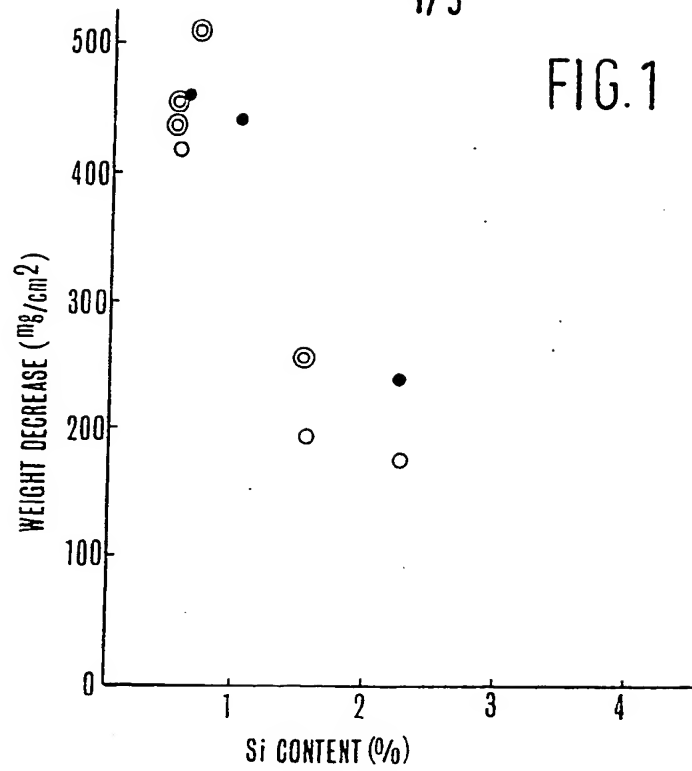


FIG.2

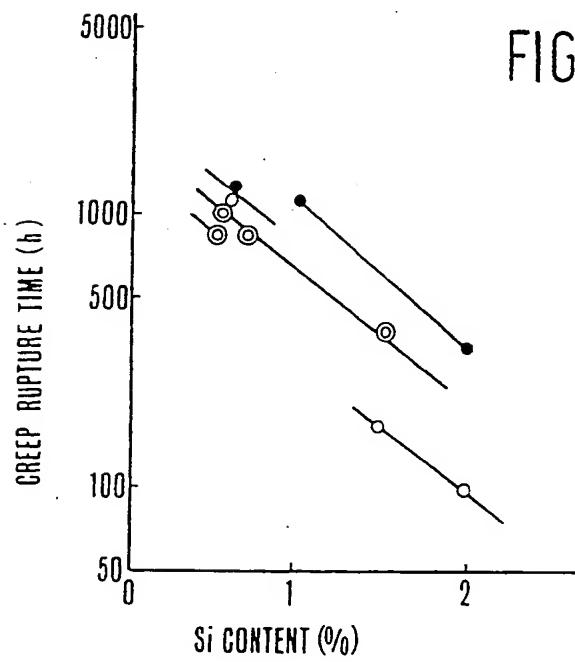


FIG. 3

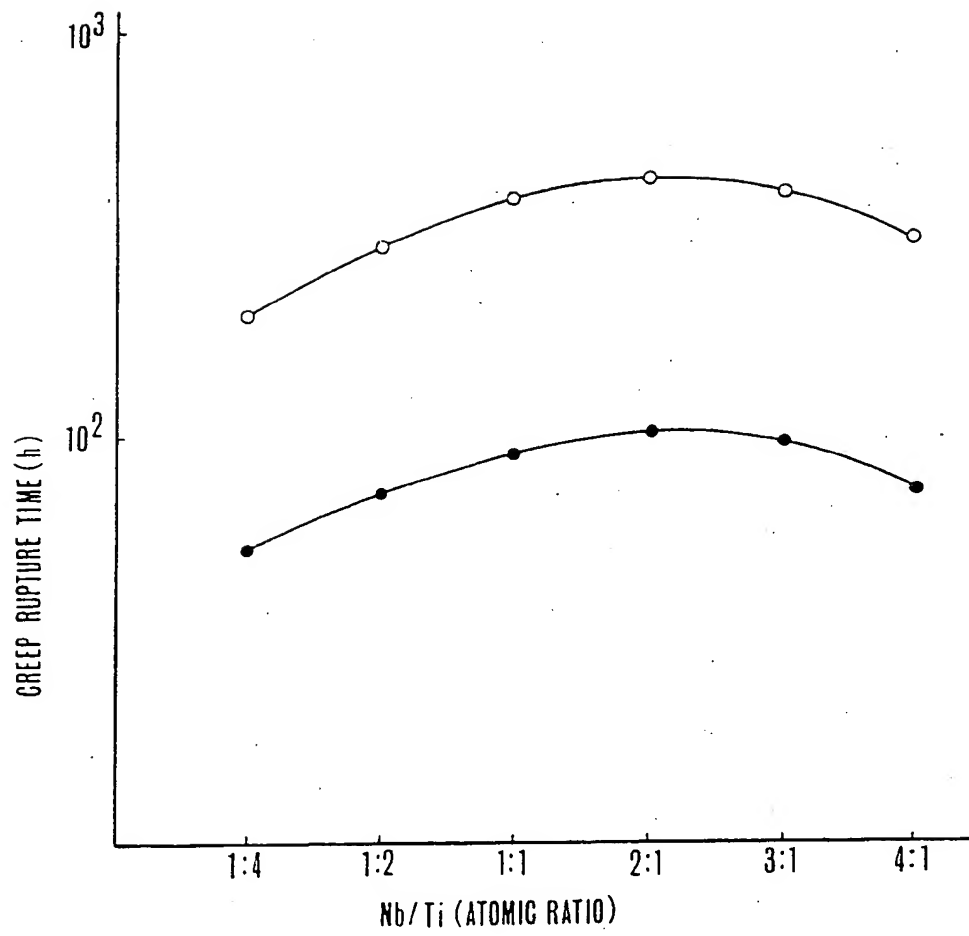
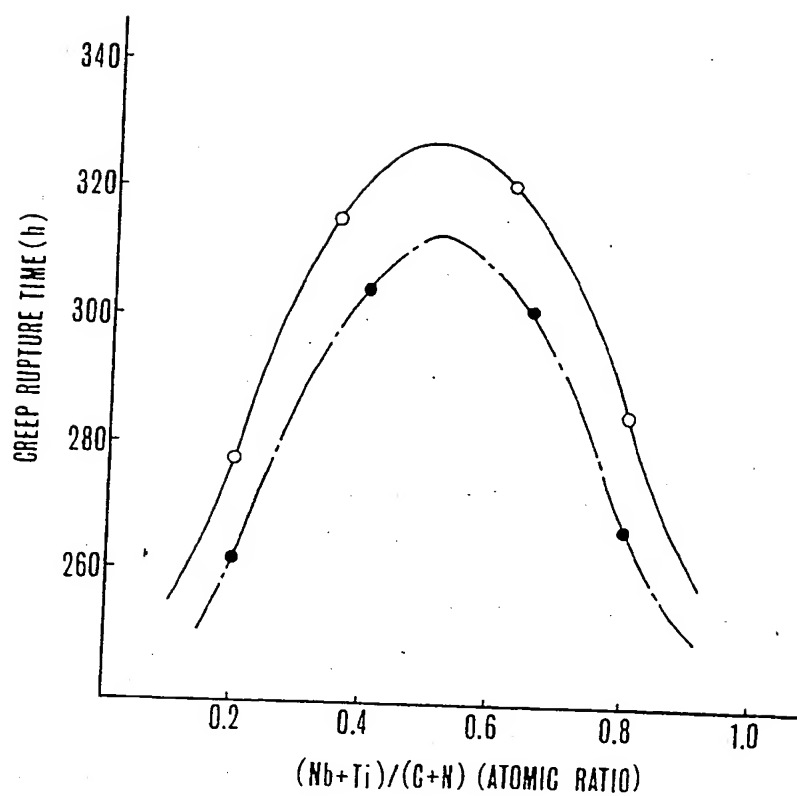


FIG. 4



## SPECIFICATION

### Austenitic heat-resistant alloys

- 5 The present invention relates to austenitic heat-resistant alloys having excellent resistance to embrittlement and corrosion at high temperatures and excellent weldability. 5

Since the "oil crisis" of 1974, the proportion of the fuel cost in the overall costs of electric power production has been increasing due to the increase in the price of fuels, such as crude oil. As a result, there have been various proposals in the U.S.A. to operate the turbines of fuel-burning power plants at higher temperatures and under higher pressures, in order to reduce the effect of fuel price increases. 10

In Japan, which has been confronted more severely than the U.S.A. with higher fuel prices, it is foreseeable that power plants will be required to operate at much higher temperatures and under much higher pressures. In this connection, it has generally been estimated that the production efficiency of a power plant will be raised by increasing the operating temperature and pressure and, for example, about a 7% increase in efficiency may be obtained by increasing the presently used operating temperature of 538° up to 650°C and vapour pressure of 3500 psig (24.13 MPa above atmospheric pressure) up to 5000 psig (34.47 MPa above atmospheric pressure). Therefore, to meet these tendencies, heat-resistant alloys suitable for boilers operable under such severe temperature and pressure conditions are needed and in fact various development efforts have been directed thereto. 15 20

In power plants where the operation is at a vapour temperature of about 650°C the boilers are subjected to temperatures of about 720°C, at which conventional heat-resistant steel materials including austenitic stainless steels, such as SUS347 (AISI 347), SUS 316 (AISI 316) and SUS 310 (AISI 310), cannot maintain the required strength, and better grades of heat resistant steel are needed. The conventional austenitic stainless steels, for example SUS 347 and SUS 316 in particular, were initially developed with a predominant consideration given to corrosion resistance at ordinary temperatures, and therefore their chemical composition may still be improved so as to produce new heat-resistant alloys which can satisfy the requirements of boiler tubes with respect to high temperature strength and corrosion resistance at elevated temperatures, as well as weldability and so on. 25 30

Steel compositions developed for such applications have been proposed, as disclosed in Japanese Laid-Open Patent Application No. Sho 52-149213. The prior art steel composition, however, has a relatively low content of Ni, from 6.8 to 20%, so that this steel composition is likely to be susceptible to the  $\sigma$  phase formation which produces adverse effects on the embrittlement characteristics of austenitic heat-resistant stainless steels when heated to high temperatures for a long period of time. Therefore, this prior art steel composition cannot be used for the new applications, as mentioned above. 35

A principal object of the present invention is to provide a new heat-resistant alloy compositions which displays better characteristics than the known steel compositions, when used in the demanding applications referred to above. 40

Accordingly, this invention provides an austenitic heat-resistant alloy composition which consists of (by weight):

45	0.02	-0.15%	C	45
	0.3	-2.0%	Si	
	0.3	-1.5%	Mn	
	.18	-25%	Cr	
	20.5	-50%	Ni	
50	0.5	-3.0%	Mo	50
	0.03	-0.3%	Ti	
	0.05	-0.6%	Nb	
	0.003	-0.01%	B	
	no more than 0.04% P			
55	no more than 0.005% S, and optionally 0.02-0.3% N			55

with the balance being iron and unavoidable impurities, which alloy composition satisfies the conditions:

- 60 Nb/Ti = 0.5-3 (atomic ratio), and (Nb + Ti)/(C + N) = 0.2-0.85 (atomic ratio). 60

The percentages are by weight in the following, unless otherwise specified.

This invention will now be described in greater detail and certain specific Examples thereof given, reference being made to the accompanying drawings, in which:-

- 65 Figure 1 shows the correlation between the alloy Si contents and the weight decrease in a 65

corrosion test;

Figure 2 shows the correlation between the alloy Si contents and the creep rupture time;

Figure 3 shows the correlation between the atomic ratio  $\text{Nb/Ti}$  and the creep rupture time;

and

Figure 4 shows the correlation between the atomic ratio  $(\text{Nb} + \text{Ti})/(\text{C} + \text{N})$  and the creep rupture time.

Initially, the reasons for the specific limitations of the component elements of the alloy composition of this invention will be explained.

Carbon has a great influence on the creep rupture strength or the rupture elongation, depending on the shape and distribution of carbides. Therefore, carbon should be present at least in a minimum amount required for forming carbides with Cr, Mo, Ti, B and Nb, which are favourable for the creep properties. On the other hand the carbon content should be maintained as low as possible in order to prevent micro-cracking at high temperatures during welding. For these reasons, the carbon content should be in a range of from 0.02%, but preferably from 0.05% to 0.15%.

The silicon content is specified to be in a range of from 0.3 to 2.0% on the basis of the results of the following experiments.

Referring to Fig. 1, this shows the results of high temperature corrosion tests conducted in synthetic ash at 650°C for 200 hours, using alloy compositions containing 0.08% C, 1.0% Mn, different Cr contents of 16% (marked by  $\odot$ ), 19% (marked by  $\bullet$ ) and 22% (marked by  $\circ$ ), 35% Ni, 1.5% Mo, 0.2% Ti, 0.2% Nb, 0.005% B, 0.02% P, 0.002% S, with various silicon contents. These tests reveal that an increased silicon content markedly reduces the corrosion rate at high temperatures. On the other hand, the same alloy compositions with similarly various silicon contents were subjected to creep rupture tests at 700°C and the results, as shown in Fig. 2, show that the high temperature creep strength decreases as the silicon content increases, irrespective of the chromium content.

Based on the discoveries shown in Figs. 1 and 2, an addition of silicon is essential for the high-temperature corrosion resistance, and for maintaining the corrosion resistance at the same level as that of SUS 347 type stainless steel, at least 0.3% Si, but preferably at least 0.4%, should be present. However, an excessive silicon content will decrease the creep rupture strength and so to maintain the high temperature creep rupture strength at the same level as that expected for SUS 347 type stainless steel, the silicon content should be no greater than 2%. For these reasons, the silicon content is limited to the range of from 0.3 to 2.0% in the present invention. Preferably, the silicon content should be maintained at 1.5% or lower, because a silicon content exceeding 1.5% will produce no substantial improvement in the high-temperature corrosion resistance.

Manganese addition is required for satisfactory deoxidation of the alloy and for obtaining sound alloy ingots, and is also effective to fix the sulphur present as impurities in the alloy so preventing hot embrittlement and improving the weldability and the hot workability. For these reasons, at least 0.3% Mn, but preferably at least 0.8%, is required. However, excessive manganese contents will deteriorate the oxidation resistance. Therefore, in the present invention, the manganese content is limited to 1.5%, and preferably 1.3% max.

Chromium is effective to improve the high-temperature creep rupture strength and oxidation resistance, and thus is an essential element for heat-resistant alloys. For a high-temperature oxidation resistance equal to or better than that of SUS 347, at least 18% Cr is required. However, too much chromium tends to cause  $\sigma$  embrittlement in the alloy when subjected to a long term heating. Therefore, the upper limit of the chromium content is set at 25% in the present invention in order to maintain a better resistance to  $\sigma$  embrittlement than 25Cr-20Ni austenitic stainless steels (SUS 310).

Nickel, when contained in amounts of more than 10% converts the crystal structure of the alloy from a body-centered cubic structure to a face-centred cubic structure, and for this reason nickel is an essential element for providing high temperature strength. Boiler tubes made of high-Cr heat-resistant steels are susceptible to  $\sigma$  embrittlement when exposed to elevated temperatures for long periods, and so at least 20.5% Ni, and preferably 24% or more, should be added to prevent  $\sigma$  embrittlement. On the other hand, too great a nickel content will stabilize the austenite and lead to easy work-hardening, and hence deteriorate the hot workability. Also, an excessive Ni content will inevitably raise the production cost. For these reasons, the upper limit of the nickel content is set at 50% in the present invention.

Molybdenum is essential for increasing the creep rupture strength through solid solution hardening and precipitation hardening effects, and for this purpose at least 0.5% Mo is required, and preferably at least 1.4% Mo should be present. Meanwhile, molybdenum tends to promote the formation of  $\sigma$  phase, thus rendering the alloy more susceptible to embrittlement and deteriorating the corrosion resistance at elevated temperatures when exposed to a long term heating. For these reasons, the upper limit of the molybdenum content is set at 3.0%, preferably 2.5%. Both of titanium and niobium, which are carbide and nitride formers, are

generally accepted to be effective at improving the creep rupture property.

The present inventors have conducted extensive studies with various proportions of Ti and Nb and have found results quite different from the conventional thinking. Fig. 3 shows the results of creep rupture tests with 12 kgf/mm<sup>2</sup> at 750°C, using two alloy systems containing different silicon contents 0.5% Si (marked by O) and 2.0% Si (marked by ●). 0.1% C, 1.0% Mn, 20% Cr, 25% Ni, 1.4% Mo, 0.005% B, 0.02% P and 0.003% S, with various atomic ratios of Nb/Ti. The creep rupture strength increases as the proportion of Nb is increased until the atomic ratio of Nb/Ti reaches about 3. This is quite contrary to the conventional thinking, as taught by Japanese Patent Publication No. Sho 50-3967, that the creep rupture strength becomes highest at the atomic ratio 1:1 of Nb/Ti.

It has been concluded from the results shown in Fig. 3 that decreased proportions of Nb in the atomic ratio of Nb/Ti cause a decrease in creep rupture strength, and the Nb content should be at least 1/2 or more of the Ti content, in atomic ratio. Preferably, the Nb content should be equal to or more than the Ti content. Also as understood from Fig. 3, with Nb contents exceeding the atomic ratio 3 of Nb/Ti, no substantial increase in the creep rupture strength can be expected. Therefore, the Nb content should be maintained at no more than three times the Ti content, in atomic ratio.

Also Ti and Nb improve the creep rupture property through the formation of precipitates with carbon or with carbon and nitrogen. Hence the proper additions of Nb and Ti are dependent on the relation between the carbon and nitrogen contents:  $(Nb + Ti)/(C + N)$ .

The creep rupture strength level varies when the carbon content or the carbon and nitrogen (C + N) content alone is changed. Therefore, an investigation of the correlation of the creep rupture strength with the ratio  $(Nb + Ti)/(C + N)$  by changing the Nb + Ti content and the C content or (C + N) content will fail accurately to determine the effect of the  $(Nb + Ti)/(C + N)$  on the creep rupture strength, because the effect of the atomic ratio Nb/Ti and the effect of the carbon content or the carbon and nitrogen (C + N) content overlap each other. In view of this consideration, the present inventors have tried to clarify the effects on the creep rupture property by maintaining the carbon content or the carbon and nitrogen (C + N) content at a constant level and changing the niobium and titanium (Nb + Ti) content, hence changing the ratio  $(Nb + Ti)/(C + N)$ .

Thus, referring to Fig. 4, the creep rupture tests with 12 kgf/mm<sup>2</sup> at 750°C were performed on two alloy systems having different nitrogen contents: 0.05% N (marked by o) and 0.005% N (marked by ●) and both containing 0.1% C, 0.5% Si, 1.0% Mn, 20% Cr, 25% Ni, 1.0% Mo, 0.005% B, 0.02% P and 0.003% S with various atomic ratios of  $(Nb + Ti)/(C + N)$ , to determine the creep rupture time of the two alloy systems. It has been concluded from the results of the tests that in the above alloy systems, the atomic ratio of  $(Nb + Ti)/(C + N)$  should be maintained in a range of from 0.2 to 0.85. If the ratio is higher than 0.85, the precipitates containing Nb and Ti are very likely to grow coarse, thus partially decreasing the effect of improving the creep rupture property, and on the other hand, if the ratio is lower than 0.2, no substantial effect of Nb and Ti will be obtained. Therefore, in the present invention, the amount of (Nb + Ti) should be in a range corresponding to the atomic ratio  $(Nb + Ti)/(C + N)$  ranging from 0.2 to 0.85, and the atomic ratio of (Nb/Ti) should be in the range of from 0.5 to 3, preferably 1 to 3, when the carbon and nitrogen contents are maintained constant, as explained hereinbefore.

In view of the above discoveries, the upper limit of the niobium content in the alloy according to the present invention is set at 0.6%, but preferably at 0.5%, and the upper limit of the titanium content is set at 0.3%, but preferably at 0.25%. Further in order to assure the favourable effects of Ti and Nb on the creep property, the titanium content should not be less than 0.03%, but preferably not less than 0.05%, and the niobium content should not be less than 0.05%, but preferably not less than 0.06%.

Boron should be present in amounts of not less than 0.003% in order to increase the creep rupture strength, but excessive boron contents will decrease the weldability and the ductility. Therefore, in the present invention, the upper limit of the boron content is set at 0.010%, but preferably 0.007%.

Phosphorus, when contained in excessive amounts, will promote precipitates, thus promoting embrittlement during creep. Therefore, in the present invention, the upper limit of the phosphorus content is set at 0.04%.

Sulphur, when present in excessive amounts, will segregate at the grain-boundaries and promote grain-boundary embrittlement during creep. Therefore, the upper limit of the sulphur content is set at 0.005%.

Nitrogen is an element conventionally known to be effective at increasing the high temperature creep rupture strength of high-Cr, high-Ni austenitic alloys, through the formation of nitrides. In order to increase the creep rupture strength through nitride formation, the nitrogen content should be no less than 0.02%, and preferably no less than 0.05%. On the other hand, increased nitrogen contents will decrease the creep rupture elongation, and nitrogen contents in

excess of 0.3% will produce no substantial increase in the long term creep rupture strength. For these reasons, the upper limit of the nitrogen content in the present invention is set at 0.3%.

Examples of the present invention will now be set out.

Table 1 shows chemical compositions of alloys of this invention and various comparative alloys. All these alloys were subjected to creep rupture tests with 12 kgf/mm<sup>2</sup> at 750°C, and Table 2 shows the results of these tests as the creep rupture time and the creep rupture elongation, as well as the atomic ratios of  $(Nb + Ti)/(C + N)$  and  $Nb/Ti$  of the alloys.

Alloys E, K, L, W, X, and B' shown in Table 1 correspond to a basic alloy composition according to the present invention, and alloys F, O, P, Q, R, T, U and A' correspond to modifications of the present invention.

Alloy A corresponds to SUS 347 and alloy B to SUS 304. Alloy C has a basic composition of 25Ni-20Cr without any addition of Ti, Nb, B and N, and alloy D has the same basic composition with no addition of B and N. Alloy E has the basic alloy composition containing Ti, Nb and B but containing no N, with the atomic ratio of  $(Nb + Ti)/(C + N)$  maintained at 0.5 and the atomic ratio of  $Nb/Ti$  maintained at 1.0. This alloy shows a higher creep rupture strength than alloys A, B, C and D due to the addition of Nb, Ti and B. Alloy F has the same alloy composition as alloy E except for the addition of N and shows a higher creep rupture strength than alloy E due to the addition of 0.06% N. Alloy G contains C in an amount exceeding the upper limit of the carbon content according to the present invention, and shows a lower creep rupture strength and a lower creep rupture elongation as compared with alloy F.

Alloy H contains Si in an amount exceeding the upper limit for the silicon content according to the present invention and shows a marked decrease in creep rupture strength due to the excessive silicon content. Alloy I contains an excessive amount of Cr. Therefore, despite the relatively high nickel content of 29.6%, it shows a lower creep rupture strength than alloy F which is within the scope of the present invention. When the chromium content exceeds 25%, as in the case of alloy I, the creep rupture property is deteriorated by carbides and intermetallic compounds such as  $\sigma$  phase.

In alloys J, K, L and M, the atomic ratio of  $Nb/Ti$  is maintained at 0.25, 0.5, 3.0 and 4.0 respectively and the atomic ratio of  $(Nb + Ti)/(C + N)$  is maintained within the range of from 0.23 to 0.58 without addition of nitrogen. As shown, when the atomic ratio of  $Nb/Ti$  exceed the upper limit of 3 as defined in the present invention, for example, 4.0 in alloy M, not only the creep rupture strength but also the creep rupture elongation are deteriorated. On the other hand, as with alloy J, when the ratio is lower than the lower limit of 0.5 as defined in the present invention, the creep rupture strength is low. In alloys N, O and P the atomic ratio of  $(Nb + Ti)/(C + N)$  is maintained within the range of from 0.33 to 0.38 with the addition of nitrogen and the atomic ratio of  $Nb/Ti$  is maintained at 0.25, 0.5 and 3.0 respectively. Alloy N, having the atomic ratio of  $Nb/Ti$  of 0.25, shows a lower creep strength as compared with alloys O and P having the ratios of 0.5 and 3.0 respectively, within the scope of the present invention. In alloys Q, R, S and W, X, Y, the atomic ratio of  $Nb/Ti$  is maintained in the range of from 0.8 to 1.1 and the atomic ratio of  $(Nb + Ti)/(C + N)$  is varied in the range of from 0.20 to 0.91, with the addition of nitrogen in alloys Q, R and S, but without the addition of nitrogen in alloys W, X and Y. Both alloys S and Y, having atomic ratios of  $(Nb + Ti)/(C + N)$  as 0.91 and 0.90 respectively, show lower creep rupture strength and creep rupture elongation than alloys Q, R, W and X having the atomic ratio within the range of from 0.2 to 0.85 as defined by the present invention.



TABLE 1

Chemical Compositions (by weight %)											
C	Si	Mn	Cr	Ni	Mo	Ti	Nb	B	N	P	S
*A	0.050	0.49	1.36	18.3	11.3	-	0.98	-	0.008	0.014	0.005
*B	0.050	0.65	0.97	18.2	9.1	-	-	-	0.007	0.015	0.004
*C	0.092	0.51	1.03	20.4	25.5	-	-	-	0.005	0.018	0.004
*D	0.094	0.51	0.99	19.1	25.1	-	-	-	0.005	0.016	0.003
E	0.098	0.53	1.01	21.0	25.3	0.095	0.21	0.0043	0.0048	0.017	0.003
F	0.097	0.50	1.04	20.9	25.6	0.094	0.22	0.0044	0.060	0.019	0.002
*G	0.155	0.49	1.03	20.1	25.1	0.096	0.20	0.0041	0.0611	0.015	0.002
*H	0.091	2.40	1.02	20.8	26.1	0.095	0.20	0.0039	0.0476	0.017	0.003
*I	0.101	0.52	1.03	26.0	29.6	0.110	0.21	0.0034	0.0624	0.015	0.003
J	0.095	0.54	1.03	21.2	26.1	0.100	0.04	0.0048	0.0050	0.020	0.002
K	0.089	0.49	1.05	20.3	25.4	0.072	0.080	0.0031	0.0048	0.018	0.003
L	0.090	0.53	1.05	21.1	24.5	0.053	0.30	0.0049	0.0051	0.019	0.002
*M	0.100	0.54	1.08	22.3	24.8	0.048	0.38	0.0052	0.0053	0.018	0.003
*N	0.096	0.51	1.07	20.8	25.7	0.153	0.069	0.0050	0.0501	0.020	0.002
O	0.099	0.52	1.02	21.0	25.6	0.130	0.130	0.0040	0.0582	0.020	0.002
P	0.092	0.51	1.08	20.7	25.4	0.051	0.30	0.0045	0.0520	0.014	0.002
Q	0.100	0.53	1.03	21.5	25.6	0.062	0.11	0.0046	0.0580	0.020	0.002
R	0.097	0.52	1.02	20.9	26.0	0.250	0.39	0.0074	0.0566	0.016	0.003
*S	0.095	0.53	1.03	20.7	25.1	0.250	0.44	0.0130	0.0413	0.018	0.003
T	0.051	0.51	1.02	20.7	25.6	0.098	0.20	0.0051	0.107	0.021	0.002
U	0.052	0.53	0.97	20.6	25.4	0.091	0.19	0.0051	0.17	0.024	0.002
*V	0.054	0.52	1.01	20.3	25.4	0.12	0.24	0.0049	0.389	0.020	0.002
W	0.060	0.49	1.10	20.5	25.2	0.03	0.059	0.0050	0.006	0.021	0.003
X	0.054	0.50	1.05	20.3	25.1	0.095	0.190	0.0051	0.005	0.019	0.003
*Y	0.049	0.51	1.03	20.1	25.3	0.090	0.190	0.0048	0.004	0.023	0.002
A'	0.050	0.51	1.01	25.0	35.0	0.071	0.27	0.0051	0.0631	0.019	0.002
B'	0.120	1.35	0.86	24.8	48.2	0.12	0.51	0.0049	0.0185	0.018	0.004

Note: "0" indicates a comparative alloy.

TABLE 2

5	Atomic Ratios		Creep Rupture Property (750°C 12kgf/mm <sup>2</sup> )		5
	Nb + Ti C + N	Nb/Ti	Rupture time(h)	Rupture elongation(%)	
10	*A	—	90	61.2	10
	*B	—	60	68.3	
	*C	—	150	50.1	
	*D	0.51	206	50.5	
15	E	0.50	318	45.1	15
	F	0.33	325	46.8	
	*G	0.24	265	40.1	
	*H	0.41	50	73.5	
	*I	0.33	86	56.8	
20	J	0.23	205	58.3	20
	K	0.32	285	65.3	
	L	0.55	291	63.1	
	*M	0.58	275	59.3	
	*N	0.34	227	62.3	
25	O	0.33	312	67.5	25
	P	0.38	280	65.2	
	Q	0.20	278	59.0	
	R	0.78	300	82.0	
	*S	0.91	250	52.3	
30	T	0.35	521	96.6	30
	U	0.24	702	80.2	
	*V	0.16	712	60.3	
	W	0.23	251	60.2	
	X	0.83	285	78.5	
35	*Y	0.90	225	55.2	35
	A'	0.50	285	55.9	
	B'	0.71	512	78.8	

Note: "\*" indicates a comparative alloy.

## CLAIMS

1. An austenitic heat-resistant alloy composition consisting of (by weight):

45	0.02	-0.15%	C	45
	0.3	-2.0%	Si	
	0.3	-1.5%	Mn	
	18	-25%	Cr	
	20.5	-50%	Ni	
50	0.5	-3.0%	Mo	50
	0.03	-0.3%	Ti	
	0.05	-0.6%	Nb	
	0.003	-0.01%	B	
	no more than 0.04% P			
55	no more than 0.005% S			55

with the balance being iron and unavoidable impurities, which alloy composition satisfies the conditions:

Nb/Ti = 0.5-3 (atomic ratio), and

60 (Nb + Ti)/(C + N) = 0.2-0.85 (atomic ratio).

2. A modification of the austenitic heat-resistant alloy composition according to claim 1, which further contains 0.02-0.3% N.

3. An alloy composition according to claim 1 or claim 2, wherein the C content is from 0.05% to 0.15%.

65 4. An alloy composition according to any of the preceding claims, wherein the Si content is 65

- from 0.4% to 1.5%.
5. An alloy composition according to any of the preceding claims, wherein the Mn content is from 0.8% to 1.3%.
6. An alloy composition according to any of the preceding claims, wherein the Ni content is from 24% to 50%. 5
7. An alloy composition according to any of the preceding claims, wherein the Mo content is from 1.4% to 2.5%.
8. An alloy composition according to any of the preceding claims, wherein the Ti content is from 0.05% to 0.25%.
- 10 9. An alloy composition according to any of the preceding claims, wherein the Nb content is from 0.06% to 0.5%. 10
10. An alloy composition according to any of the preceding claims, wherein the B content is from 0.003% to 0.01%.
11. An austenitic heat-resistant alloy composition consisting of (by weight):
- |    |                           |         |    |    |
|----|---------------------------|---------|----|----|
| 15 | 0.05                      | -0.15%  | C  | 15 |
|    | 0.4                       | -1.5%   | Si |    |
|    | 0.8                       | -1.3%   | Mn |    |
|    | 18                        | -25%    | Cr |    |
| 20 | 24.0                      | -50%    | Ni | 20 |
|    | 1.4                       | -2.5%   | Mo |    |
|    | 0.05                      | -0.25%  | Ti |    |
|    | 0.06                      | -0.5%   | Nb |    |
|    | 0.003                     | -0.007% | B  |    |
| 25 | no more than 0.04% P      |         |    | 25 |
|    | no more than 0.005% S and |         |    |    |
|    | 0.05-0.3% N               |         |    |    |
- with the balance being iron and unavoidable impurities, and satisfying the conditions:
- 30  $Nb/Ti = 1-3$  (atomic ratio), and 30
- $(Nb + Ti)/(C + N) = 0.2-0.85$  (atomic ratio).
12. An alloy composition according to any of claims 1 to 10 or according to claim 11 and substantially as hereinbefore described in the Examples.

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